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Bond Ionicity in Halogen Silver Interaction

by

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BOND IONICITY IN HALOGEN SILVER INTERACTION

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SUMMARY

The nature of the bonding between halogen atoms (F, Cl and Br) and the Ag (111) surface has been investigated by analyzing ab initio Hartree-Fock wave functions for cluster models of the Ag surface and a halogen atom. Using a variety of criteria, we conclude that the bonding is ionic and that the halogen ionicity is essentially -1. The measures of ionicity reported are a) the expectation value of a projection operator which provides an indication of the total charge associated with the halogen atom, b) the analysis of the dipole moment curve as function of distance, c) the effect on the equilibrium bond distances of an uniform external electric field, and d) the decomposition of the interaction energy into the sum of different contributions. This latter analysis shows that the bonding arises, almost entirely, from the Coulomb attraction between the charged halogen and the metal and from polarization of the two sub-units.

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I. INTRODUCTION

The interaction of halogen atoms with Ag surfaces has been studied for well defined Ag(111) surfaces in ultra-high vacuum, UHV, and on Ag electrodes in electrochemical environments. For Cl/Ag(111), Lambie et al.¹ have used surface extended X-ray absorption fine structure, SEXAFS, to determine the surface structure for 1/3 of a monolayer, ML, and 2/3-ML of Cl. For both coverages, they find that Cl is at a three-fold site at a vertical distance of 4.13 a.u. above the Ag surface. In addition, in situ SEXAFS measurements of bromide adsorbed on Ag(111) electrodes at full coverage were recently performed and Ag-Br bond distances determined.² Adsorption of chloride, bromide and iodide (fluoride does not contact adsorb from aqueous solutions because it is highly hydrated) on polycrystalline noble metal electrodes has been extensively studied.³⁻⁷ In some cases both coverage and electrosorption valence (essentially charge on the adsorbed ion) were determined. However, there is little agreement on electrosorption valence perhaps due to differences in experimental method and conditions. The interpretation of these measurements to obtain the adsorbate ionicity requires several assumptions and detailed theoretical modeling of what happens as an ion approaches a surface would be very valuable.

The primary purpose of the cluster model studies described in this paper is to establish the nature of the bonding of halogen atoms, F, Cl, and Br, chemisorbed on a Ag(111) surface. We find the bonding is unequivocally established, through several different criteria, to be ionic; the adsorbate halogen carries essentially a charge of -1. The criteria for establishing the ionic character of the bonding have been developed in a series of recent papers.⁸⁻¹⁰ These include: (1) Projection of the halogen character on the total cluster wavefunction. (2) Analysis of the dipole moment curve as a function of the distance of the halogen from the Ag surface. (3) Use of a Constrained Space Orbital Variation,¹¹ CSOV, analysis to separately characterize the importance of intra-unit polarizations and inter-unit charge flow and covalent bonding. And (4) the effect of an applied external

electric field on the equilibrium distance of the halogen from the surface. These criteria are not subject to the artifacts which arise from the more commonly used Mulliken population analysis.¹² Taken together, they give a consistent view and strong evidence for an ionic bond for all of the halogens considered, F, Cl, and Br.

In the following section, Sec. II, we describe the features of the cluster model and the molecular orbital, MO, wavefunction. For all cases, we consider adsorption at the eclipsed, tetrahedral, three-fold site of Ag(111). In Sec. III, we present the evidence given by all four criteria for the ionic character of the adsorbed halogen. In Sec. IV, we consider adsorption of F on clusters modeling the octahedral three-hollow site of Ag(111). Finally in Sec. V, our conclusions are summarized.

II. WAVEFUNCTION DETERMINATION

The Ag_4X cluster, $\text{X}=\text{F}, \text{Cl}, \text{Br}$, is used to model the interaction of X with Ag at a three-fold tetrahedral site of the Ag(111) surface; see Fig. 1. A three-fold site for adsorption is reasonable and is supported by experimental data (see, for example, Ref. 1). This cluster contains the nearest Ag neighbors of the halogen; these are the atoms that are most directly involved in the Ag-X bond. For the Ag atoms, an Effective Core Potential (ECP)¹³ has been used; the 28 electrons from the deep core 1s to 3d shells are represented by the ECP while the 19 electrons arising from the 4s, 4p, 4d and 5s shells are explicitly included in the wavefunction. We call this operator a 19 electron ECP to distinguish it from an ECP which explicitly includes only the 11 Ag electrons from the 4d and 5s shells, an 11 electron ECP¹⁴ and from an ECP which includes only the outermost 5s electron, a 1 electron ECP¹⁵. The 11 and the 1 electron Ag ECP's have also been used, in particular for larger clusters, as will be discussed below. For the halogens, all electrons are included in the SCF cluster wavefunctions.

The molecular wavefunctions have been determined using flexible basis sets of contracted Gaussian type orbitals, GTO's. The valence

basis set for Ag has been contracted to 4s4p3d; see Ref. 13 for the GTO exponents and the ECP parameters. The basis sets for the halogen atoms, optimized for the neutral atoms,¹⁶⁻¹⁸ were extended with diffuse s, p, and d functions whose exponents have been determined in order to obtain a better approximation for the SCF electron affinity¹⁹ (EA), and for the dipole polarizability,²⁰ α_0 , of the anions. The neutral halogen basis sets are denoted as basic while the basis set with the added functions are denoted extended. The halogen GTO basis sets, exponents and contraction coefficients, are given in Table 1. In Table 2, the values of the halogen EA and α_0 computed with the present basis set are compared to Hartree-Fock limit values^{19,20} and, for the EA's, to experiment.²¹ The computed EA values are very close to the Hartree-Fock limit values,¹⁹ but differ substantially from the corresponding experimental ones (Table II). The lack of correlation effects is the main reason for this discrepancy.²² For α_0 , our calculated values with the extended halogen basis set are 25-30% smaller than the Hartree-Fock limit.²⁰ However, they do reproduce the large increase in α_0 going from F⁻ to Cl⁻ to Br⁻. If the basic halogen basis sets are used and the diffuse GTO's are not included, the α_0 's are very small; see Table II.

For all clusters considered, the halogen atom to surface distance has been varied along the C_{3v} axis to give a potential energy and a dipole moment curves.

It is possible for the Ag₄X cluster calculations that the Ag atom basis functions may improve the description of the halogen atom properties. This may be true in particular for the α_0 where, as we have shown, the values with the extended basis set differ by significant amounts from the Hartree-Fock limit values. This basis set superposition error, BSSE, may introduce artifacts in the analysis of the halogen-Ag interaction.¹² We estimate the BSSE by computing α_0 for the halogen anions using the full basis set of the four Ag atoms in Ag₄X as well as the halogen basis. The Ag basis sets are placed at the positions that the Ag atoms would have near the calculated equilibrium distance of the halogen from the Ag₄ cluster. With the ghost basis sets, we compute the BSSE α_0 values from the change in the halogen anion energy due

to a uniform electric field²³ $\Delta E = - 1/\alpha_D F^2$. The BSSE values for the extended halogen basis set are given in Table II. The BSSE leads to a modest improvement of the α_D ; we shall show later that the uncertainty of the analysis for the halogen-Ag interaction due to this BSSE is not large.

For distances close to the equilibrium Ag-halogen distance, the ground state configuration of Ag_4X is $(1a_1)^2 (2a_1)^2 (3a_1)^2 (1e)^4 (2e)^1 (2E)$; the halogen cores as well as the Ag $1s^2$ to $4d^{10}$ cores are not given explicitly. This state arises from the combination of the Ag_4 ground state $(a_1)^2 (e)^2$ with the seven valence ns and np electrons of X in configuration $(a_1)^2 (a_1)^2 (e)^3$. The main bonding effects are in the outer e shells and can be either covalent or ionic. In the latter case, the bonding can be considered as originating from the interaction of the ionized Ag_4^+ $(a_1)^2 (e)^1$ cluster and the closed shell anion X^- $(a_1)^2 (a_1)^2 (e)^4$. In the covalent view, a filled bonding $(1e)^4$ and a singly occupied antibonding $(2e)^1$ MOs are formed.

Properties of the Ag_4X interaction are given in Table III. These include the equilibrium distance of X above the Ag surface plane, z_e , the dipole moment at z_e , μ_e , the vibrational frequency, ω_e , the anharmonicity,²⁴ $\omega_e x_e$, and the dissociation energy, D_e . The ω_e and $\omega_e x_e$ are computed by matching a fourth degree polynomial expansion of the potential energy curve for the points on the curve near z_e . The D_e is computed with respect to either dissociation to neutral units, Ag_4 and X, denoted $D_e(Ag_4+X)$, or dissociation to ionic units, Ag_4^+ and X^- , denoted $D_e(Ag_4^++X^-)$. When a bond has a large degree of ionic character Hartree-Fock values of D_e with respect to neutrals may have a large error because the Hartree-Fock ionization potential, IP, and EA are not accurate. In this case, it has been shown²⁵ that D_e with respect to the ionic limits corrected by experimental value for the IP and EA of the dissociation products gives quite accurate values for the D_e . It is worth noting that the computed bond distance for Cl on Ag(111), an Ag-Cl distance of 2.84 Å, is closer but somewhat larger than the value of 2.70 Å obtained from EXAFS measurements by Lamble et al.¹. Given the very shallow potential energy curve, small $\omega_e = 180 \text{ cm}^{-1}$, this is satisfactory agreement for an SCF calcu-

lation. It provides evidence for the adequacy of our cluster model.

A major concern in cluster model studies is the dependence of the chemisorption properties on the size and shape of the cluster. In order to verify the generality of the results obtained with the small Ag_4 cluster we considered a second cluster model containing 3 Ag atoms in the first layer and 7 Ag atoms in the second layer (Fig. 2); the cluster is used with a F adsorbate only. The total cluster is denoted $\text{Ag}_{10}(3,7)\text{F}$ or, simply, Ag_{10}F . In this case, the computational effort has been reduced by treating the four Ag atoms defining the tetrahedral chemisorption site with an 11 electron ECP in which the 4s and 4p electrons are not considered explicitly.¹⁴ The six neighboring Ag atoms in the second layer have been treated with a 1 electron ECP¹⁵ in which all the shells except the 5s are represented by an ECP.

The reliability of the Ag 11 electron ECP in studying halogen chemisorption has been tested comparing the results for Ag_4F obtained with the two approaches, namely including the 4s and 4p electrons in the ECP or treating them explicitly. The results, reported in Table III, indicate a substantial agreement of the two sets of calculations. This guarantees that the use of the 11 electron ECP for the study of the larger Ag_{10} cluster is possible without losing accuracy.

The bond distance and vibrational frequency determined for F on Ag_{10} (Table III) are close to those obtained with the smaller Ag_4 cluster; on the other hand, the binding energy is about 25% smaller in the Ag_{10} case. However, this result is not too surprising considering that oscillations in chemisorption energies usually occur varying the cluster size and shape, at least for relatively small clusters.²⁶ The slow convergence of D_e to the experimental value is generally related to the character and energy of the cluster frontier orbitals. In the case of ionic interactions, the important substrate cluster properties are its effective workfunction and its polarizability. The important conclusion of the comparison of Ag_4F with Ag_{10}F , as discussed in the following sections, is that the nature of the interaction is not dependent on the cluster nuclearity.

The 11 electron ECP has been used also for the investigation of $\text{Ag}_6(3,3)$ and $\text{Ag}_7(3,3,1)$ clusters interacting with F (Fig. 2). These two clusters model the octahedral three-hollow site of the Ag (111) surface and allow a comparison of this site with the tetrahedral one represented by the Ag_4 cluster. The results for these two clusters are discussed in the last section.

III.EVIDENCE FOR BOND IONICITY IN Ag-HALOGEN INTERACTION

A.Projection of Halogen Character in Ag_4X

A measure of the extent to which an orbital, φ , is occupied in a many-electron wavefunction, Ψ , is given by the expectation value, P_φ , of the projection operator, $P(\varphi)$,

$$P(\varphi) = \varphi\varphi^\dagger,$$

$$P_\varphi = \langle \Psi | P(\varphi) | \Psi \rangle. \quad (1)$$

The details given about projection operators in Ref. 8 are summarized here. The value of P_φ is not dependent on the basis set expansion used to construct Ψ ; thus, projection avoids the artifacts often associated with a population analysis.⁸ The projected orbitals, φ , are chosen to have a well defined physical significance; in this paper, orbitals of the isolated adsorbate are used. If the φ are taken to be the spatial parts of spin-orbitals and spatial degeneracy is neglected, then $P_\varphi \leq 2$. There are three cases for values for P_φ . In case I, $P_\varphi \approx 2$ and φ is completely occupied in Ψ ; in case II, $P_\varphi \approx 0$ and φ is not occupied at all. These two limiting cases have the simplest interpretation. In the third case are the intermediate values, $0 < P_\varphi < 2$, giving an indication of a covalent bond. For the analysis of this case, it is necessary to take into account the overlap between the orbitals of the isolated adsorbate and substrate when these two sub-units are superposed. To estimate the total charge on the halogen atom in Ag_4X , a sum over all the orbitals occupied in the isolated halogen anion is formed. The number of electrons given by this projection operator is denoted by N_p and the effective

charge associated with the halogen as $Q_p = Q_N - N_p$ where Q_N is the nuclear charge.

For distances near z_e , values of N_p and Q_p are given in Table IV; the projections do not change significantly for large variations of z about z_e . For all the halogens, F, Cl and Br, the ionicity given by Q_p , is essentially -1. It is worth noting that no difference is found when the Ag surface is represented by the Ag_4 or Ag_{10} clusters (Table IV). For all the individual halogen orbitals, case I or $P_\varphi \approx 2$ holds; all the halogen orbitals are fully occupied in Ag_4X . In other words, the projection gives strong evidence that Ag_4X is properly described as Ag_4^+ and X^- . Although the projection indicates a deviation from an ionicity of -1 that is trivial for F, it does suggest that there might be a covalent contribution, albeit small, for Br; this is discussed further in Section III C, below.

B. Dipole Moment Curves for Ag_4X Clusters

A commonly used way to estimate the ionicity of an adsorbate is based on the experimentally observed change in the work function, ϕ , between a clean surface and an adsorbate covered surface (see, for example, Refs. 27-29 and references therein). This approach is used because the change in ϕ is due to a change in the surface dipole to which the redistribution of charge between substrate and adsorbate makes a significant contribution. In terms of the cluster properties of Ag_4X , an estimate obtained in this way, denoted Q_D , could be given by

$$Q_D \sim [\mu(Ag_4X) - \mu(Ag_4)]/z_e, \quad (2)$$

where $\mu(Ag_4X)$ is the cluster dipole for X at equilibrium, z_e , and $\mu(Ag_4) = -0.78$ a.u. is the dipole moment of the bare cluster. Equation (2) assumes that charge is taken from the surface layer of Ag and distributed spherically about the halogen; polarization effects are neglected. In Table V, Taylor expansions about $z = z_e$ are given for the dipole moment curve as a function of z ;

$$\mu(Ag_4X; z) = M_0 + M_1(z - z_e) + M_2(z - z_e)^2 + M_3(z - z_e)^3 + \dots; \quad (3)$$

the first term, M_0 , is $\mu(\text{Ag}_4\text{X}; z_e)$. Using the values in Tables III and V, Eq. (2) leads to $Q_D(\text{F}) \sim -0.1$, $Q_D(\text{Cl}) \sim -0.2$, and $Q_D(\text{Br}) \sim -0.3$. These estimates are dramatically smaller than the $Q_p \approx -1$ given in Table IV; they suggest a covalent rather than ionic bond.

However, the linear behavior, small M_2 and M_3 , which is found for all X, is consistent with an ionic bond⁸ where the slope, M_1 , is related to the extent of ionicity. The dipole moment of two point charges $+q$ and $-q$ will be $\mu = -q \times r$ and $d\mu/dr = -q$, assuming that $-q$ is at positive r with respect to $+q$. Hence, for an ideal fully ionic molecule where $q=1$, $d\mu/dr = -1$ and the curve is a straight line. Unfortunately, it is possible to obtain two, quite different, estimates of the ionicity from the M_1 for Ag_4X . For the first, the polarization of both the Ag_4 and X sub-units is neglected; then $Q=M_1$, where Q is the effective charge of the halogen atom X. Since, for all X, the $|M_1|$ in Table V are larger than 1, this estimate of Q indicates that Rydberg levels in addition to the halogen rare gas cores are occupied; this is hardly likely. The second way of estimating the ionicity from M_1 arises from the use of image charge theory (see Ref. 29 and references therein) to describe the substrate polarization. In image charge theory, the metal electrons near a surface where a test charge or ion is present redistribute so that there is no electric field within the metal. This redistribution leads to an effective, or image, charge within the metal of opposite sign to the test charge at a distance below the image plane equal to the distance of the test charge above it; in this case, $Q = M_1/2$. This simple theory shows that the substrate polarization makes a large contribution to M_1 and explains the large $|M_1| > 1$ values in Table V.

In order to reduce this factor of two uncertainty in the estimate of the adsorbate Q , a further analysis of the dipole moment curves is required. One way to obtain additional information is to transform the Ag_4X cluster orbitals into those which are most like X, denoted $\varphi_i(\text{loc}, \text{X})$, and the orthogonal complement of the SCF canonical space to the space of $\varphi_i(\text{loc}, \text{X})$. A corresponding orbital transformation^{30,31} provides the required transformation to maximally localized orbitals. It has been performed between the

Ag_4X orbitals and the orbitals of the isolated X anion for a range of X distances z . The contribution of the $\varphi_i(\text{loc}, \text{X})$ orbitals to the total cluster dipole is denoted $\mu(\text{X})$ given by

$$\mu(\text{X}) = -\sum_i \langle \varphi_i(\text{loc}, \text{X}) | z | \varphi_i(\text{loc}, \text{X}) \rangle + Q_N Z_N; \quad (4)$$

where Q_N and Z_N are the charge and position above the surface, respectively, of the halogen nucleus. The Taylor expansion coefficients for $\mu(\text{X}; z)$ about z_e , Eq. (3), are given in Table V. The $\mu(\text{X}; z)$ curves are also linear but now the slope, M_1 , provides more direct information about the halogen ionicity.

The $M_1(\text{F}) = -1.0$ (for both Ag_4 and Ag_{10} clusters) and $M_1(\text{Cl}) \cong M_1(\text{Br}) = -1.1$ are fully consistent with the ionicity obtained from the projection of $Q_p \approx -1$. The $|M_1|$ for Cl and Br is larger than 1 because they have a modest polarizability; see α_D in Table II. The polarization of X^- by Ag_4^+ is also reflected in the value of M_0 for $\mu(\text{X})$. If the corresponding orbitals, $\varphi_i(\text{loc}, \text{X})$, were not polarized and were entirely of halogen character, the M_0 would equal $-z_e$. The presence of Ag_4^+ polarizes the X^- charge toward the surface; $|M_0|$ is $\sim 10\%$ smaller than z_e for F decreasing to $|M_0|$ being $\sim 30\%$ smaller than z_e for the more polarizable Br. It remains only to directly examine the polarization effects for Ag_4^+ ; this is done in the following sub-section.

Before closing this section, we compare, briefly, the results for Ag_4F and Ag_{10}F given in Table V. The dipole moments for Ag_{10}F at z_e and for bare Ag_{10} , $\mu(\text{Ag}_{10}) = 0.31$, give, using Eq. (2), a value for the F ionicity of $Q_D(\text{Ag}_{10}\text{F}) = 0.20$; this is similar to $Q_D(\text{Ag}_4\text{F}) = 0.09$. When the $\mu(\text{X})$ for Ag_{10}F and Ag_4F are compared, the extremely similar values of M_1 give strong evidence for a F ionicity of -1 in both Ag_4F and Ag_{10}F .

C. Different bonding contributions to the interaction energy

A detailed method of analysis, the constrained space orbital variation (CSOV), has been developed to separately measure the importance of various charge rearrangements which occur when a bond is formed.^{9,11,32} In particular, the CSOV method makes it possible to distinguish the consequences of intra-unit charge polarization and inter-unit covalent and ionic bonding. Given the strong evi-

dence, presented above, that the Ag_4X binding is ionic, the starting point of the CSOV analysis is taken as the unperturbed charge densities of the separated ionic units,⁹ the Ag_4^+ cation and the X^- anion. The anion is represented in two ways. First, by a unit point charge, $\text{PC} = -1$, placed at the position of the halogen nucleus; this models a spherical anion but neglects its spatial extent. For the second representation of the anion, the SCF orbitals of the isolated anion are superposed with the Ag_4^+ charge distribution; they are fixed and not allowed to change. However when the energy is evaluated, all interactions arising from the presence of the frozen X orbitals are taken into account, including the exchange interaction³²; the spatial extent of the spherical X^- anion is fully treated.

These two representations of the halogen anion are used for the first two steps of the CSOV process. In the first, the Ag_4^+ orbitals are fixed as they are obtained for isolated Ag_4^+ ; this wavefunction, denoted here as charge superposition, is the starting point, or step 0, of the CSOV process.¹¹ The Ag_4^+ orbitals are also allowed to vary and change because of the presence of the X anion for both the PC and extended representations of X^- ; this wavefunction, denoted Ag_4^+ variation or $V(\text{Ag}_4^+, \text{Ag}_4^+)$, is step 1 of the CSOV process. The Ag_4^+ variation takes the polarization of Ag_4^+ by the presence of the anion into account. For each wavefunction, we report the interaction energy, defined such that $E_{\text{INT}} > 0$ corresponds to attraction, as the difference of the energy of Ag_4X and the separated ionic sub-units, Ag_4^+ and X^- ; we also report the value of μ . These results are given in Tables VI-VIII; in each case a distance of X above Ag close to z_e is used.

We consider the results for Ag_4X . There is a large Coulomb attraction at the charge superposition step for both the PC and the extended X^- . Of course, the attraction for the PC will grow as it is moved closer to the surface; this does not occur for X^- because of the repulsion arising from the non-bonding overlap of the Ag_4^+ and X^- charge distributions (Pauli repulsion). For a wide range of distances about equilibrium, this repulsion varies exponentially; for Ag_4F near z_e , the Pauli repulsion taken as the difference in E_{INT} for the PC and for F^- is 1.5 eV. We describe

this as a surface "wall" effect. The overlap of the Ag_4^+ and X^- charge distributions can also be seen in the difference of μ for the PC and X^- cases at the charge superposition step. When the Ag_4^+ variation is permitted, there are large changes for E_{INT} and μ both for the PC and X^- cases. For F^- , the μ increases by ~ 3 a.u. because the Ag_4^+ electrons polarize by moving down or away from the negatively charged F^- . This large change in μ due to the Ag polarization explains the poor values of Q_D obtained from Eq. (2), where this polarization is neglected. The Ag_4^+ polarization also increases E_{INT} for Ag_4F by ~ 2.0 eV. However, the surface "wall" remains, as can be seen by comparing the PC and F^- values of E_{INT} for the Ag_4^+ variation wavefunction. Similar conclusions are obtained from the Ag_4Cl and Ag_4Br results in Tables VII and VIII.

In addition to the charge superposition and $V(Ag_4^+, Ag_4^+)$ steps discussed above, the CSOV analysis contains four additional steps. Since these steps are used to measure the importance of changes which involve the halogen occupied and virtual orbitals, the approximation of treating the halogen anion as a point charge cannot be used.

In the next step of the CSOV process, step 2 or $V(Ag_4^+, all)$, the basis for the variation of the Ag_4^+ orbitals is extended to include the X^- virtual orbitals; the X^- occupied orbitals are still held fixed. This step indicates the amount of charge transfer from Ag_4^+ to X^- . It is important to note that basis set superposition can effect the result at this step¹² since the increased basis set for Ag_4^+ can improve the description of Ag_4^+ without any charge transfer or dative bonding taking place.

In CSOV step 3, the intra-unit polarization of X^- due to the presence of Ag_4^+ is taken into account. For this step, denoted $V(X^-, X^-)$, the Ag_4^+ orbitals are fixed as they were determined at the preceeding step, $V(Ag_4^+, all)$. The X^- orbitals are varied in the halogen anion virtual space; in effect, the halogen intra-unit polarization due to the presence of the Ag_4^+ cluster cation is allowed. In the next CSOV step 4, $V(X^-, all)$, the space for the variation of the X^- orbitals is increased to include the Ag_4^+ virtual orbitals; this step allows charge donation or covalent

bonding to the $Ag\ddagger$ virtual space. As for the $V(Ag\ddagger,all)$ CSOV step 2, we must consider at this step, the possibility of BSSE artifacts.

In CSOV step 5, denoted $V(cov)$, the covalent mixing between the $V(X^-,all)$ step cluster valence e orbitals, $(1e)^4$ (X^-) and $(2e)^1$ ($Ag\ddagger$) is allowed; all other orbitals are fixed as determined in step 4. The result of step 5 is compared to the full unconstrained SCF result and if they are nearly the same this means that all important bonding contributions have been considered.

From Tables VI-VIII it is apparent that the electrostatic interaction and the $Ag\ddagger$ cluster polarization are by far the most important contributions to the bonding and that the other mechanisms do not change the interaction energy or dipole moment by large amounts. The change from $V(Ag\ddagger,Ag\ddagger)$ to $V(Ag\ddagger,all)$ is small for all X; the increase in D_e is < 0.1 eV and the decrease in μ is < -0.06 a.u.. If these changes are physical, they would require partial occupation of Rydberg orbitals of the closed shell halogen anion: it is extremely energetically unfavourable to add charge to X^- . Hence the small changes found at CSOV step 2 arise from BSSE. More significant is the energy lowering associated with the X^- polarization, CSOV step 3 or $V(X^-,X^-)$, which, of course, is larger for the more polarizable Cl and Br atoms than for F. The polarization of X^- toward the positive Ag surface leads to a positive change in μ , $\Delta\mu$.

The full space variation of the X^- charge in step 4 gives a 0.5 eV contribution to E_{INT} for Cl and Br and a 0.25 eV contribution for F coming from the X^- to $Ag\ddagger$ charge transfer. These values must be considered as upper bounds because of the basis set superposition errors. The part of the contribution to ΔE at this CSOV step due to the basis set superposition errors can be estimated in the following way. The ΔE_{INT} at CSOV step 3, $V(X^-,X^-)$, which would arise if the α_D for the free anion were the BSSE value rather than the value for the isolated with halogen extended basis set is given by

$$\Delta E_{INT} \text{ (CSOV step 3; BSSE corrected) } =$$

$$\Delta E_{INT}(\text{CSOV step 3}) \times [\alpha_D(\text{BSSE}) / \alpha_D(\text{extended basis})] \quad (5)$$

The change in ΔE_{INT} is largest for Cl where it is 0.05 eV; for F and Br, the changes are 0.03 and 0.01 eV, respectively. This change should be used as an amount to reduce the ΔE_{INT} at CSOV step 4, $V(X^-,all)$, to account for the BSSE at this step. For Cl, this correction to the Cl back-donation contribution to the covalent bonding reduces the value from the directly calculated 0.47 eV to 0.42 eV. Clearly, the $V(X^-,all)$ CSOV results in Tables VI-VIII indicate a higher degree of covalency for the Ag-Cl and Ag-Br interactions than for the Ag-F interaction even when the BSSE effects are taken into account. This result is consistent with the projection operator analysis, Table IV.

As expected from the large X^- ionicity, the e^4-e^1 covalent interaction at CSOV step 5 leads to very small changes in E_{INT} and μ . The near agreement between the full SCF and step 5 E_{INT} shows that no important bonding effects have been neglected.

The CSOV analysis clearly shows that the electrostatic interaction and the cluster polarization alone account for about 80-90 % of the whole interaction energy. The main difference between F, Cl, and Br is that, because of the larger equilibrium bond distances, the electrostatic interaction and the Ag cluster polarization are smaller for Cl and Br than for F. On the other hand, the contribution from the Cl- and Br- polarization is higher, as expected on the basis of the larger dipole polarizabilities of these anions.

D. Field effects on bond distances

A further proof of ionicity can be obtained by applying an uniform external electric field normal to the cluster surface. If the bonding is ionic, as shown by the previous analyses, the effect of the field would be that to move the negatively charged halogen up and down to an extent which depends on the sign and on the magnitude of the applied field.

The energies on the SCF potential surface for the variation of the X^- geometry in the presence of the field are denoted $E_{SCF}(F,Z)$; F is the magnitude of the electric field and Z re-

presents the ligand coordinates. The SCF variational solution is obtained with the Hamiltonian, $H(F)$

$$H(F) = H(0) + F \sum_i r_i - F \sum_i R_i \quad (6)$$

where $H(0)$ is the usual $F=0$ Hamiltonian and r_i (R_i) are the electron (nuclear) coordinates. The first order perturbation theory energy, $E_p(F,Z)$ is defined as the difference between the $F = 0$ SCF energy and $\mu \times F$, where μ is the field free dipole moment^{10,33}. The difference between $E_p(F,Z)$ and $E_{SCF}(0,Z)$ is a Stark effect^{10,33}; it does not include any chemical change induced by the field. These electronic effects are explicitly considered in the SCF variational energy in the presence of the field, $E_{SCF}(F,Z)$. Hence, the differences between Stark and SCF values for the Ag-halogen bond distances are indicative of the importance of the chemical changes occurring in the bonding by effect of the external field. In the following we refer to the equilibrium bond distances for the $E_p(F,Z)$ potential curve as Stark values and to the full variational $E_{SCF}(F,Z)$ values simply as SCF.

The fields considered are $F = \pm 0.01$ a.u. = $\pm 5.7 \times 10^7$ V/cm; this field is comparable to the fields at the electrode surface of an electrochemical cell when a potential of about 1 V is applied.³⁴ The sign convention is such that $F < 0$ attracts electrons from the surface toward the ligand. Indeed, we observe large field-induced changes in equilibrium bond distance when $F = -0.01$ is applied. The X^- ions are pulled away from the surface (Table IX) to equilibrium bond distances which are about 10% larger than for the $F = 0$ case. The ion shift follows the trend $Br > Cl > F$ consistently with the sequence of dipole moments (Table III) and originates entirely from the interaction of the cluster dipole and the field (Stark effect). When the field $F = +0.01$ is applied, the ions are pushed toward the surface but the equilibrium distances vary to a smaller extent with respect to the $F = -0.01$ case because of the increasing Pauli repulsion ("wall effect") occurring when the X^- ion approaches the cluster surface.

The very similar Stark and full variational SCF shifts in z_e provide further strong evidence that the chemical effects are

small and the bonding is dominated by the electrostatic interaction.

IV. F CHEMISORPTION ON OCTAHEDRAL SITE

The three-fold site is known to be the preferred one for chemisorption of halogens on the Ag (111) surface.¹ However, it is experimentally difficult to distinguish between the tetrahedral and the octahedral sites of the Ag(111) surface. In the tetrahedral cavity, the presence of an Ag atom directly below the halogen adsorbate can in principle allow an easy electron redistribution (polarization) following the ion formation on the surface.

The two clusters chosen to model the octahedral site, Ag₆ and Ag₇, differ for the presence in the latter of an Ag atom on the third layer (Fig. 2). The results for F chemisorption on Ag₆ and Ag₇ are given in Table X. As found for Ag₄F and Ag₁₀F clusters, also the Ag₆ and Ag₇ clusters exhibit close values for bond distances (the difference is about 1%), similar but not identical vibrational frequencies (here the difference is around 7%), but dramatically different values of the binding energies (about 0.8 eV difference for the dissociation in F⁻ and Ag_n⁺) (Table X). However, despite the different chemisorption properties for Ag₆X and Ag₇X, the nature of Ag-halogen interaction is the same for both clusters. The projection and the dipole moment analysis, Table X, indicate that the bonding is ionic and that F⁻ is formed; this is the same bonding found for the tetrahedral site with the Ag₄F and Ag₁₀F clusters.

In order to better understand the bonding mechanism in Ag₆F and Ag₇F, and therefore to rationalize the observed differences in binding energies, we performed a CSOV analysis. This analysis has been carried out in a somewhat different fashion than the more conventional CSOV analysis for the Ag₄X clusters described in Sec. III C. The different approach is taken because our primary concern is to understand the origin of the different D_e for the Ag₆F and Ag₇F clusters. The E_{INT} defined, as before, with respect to the energies of the Ag_n⁺ and F⁻ ions and the μ are given in Table XI.

The CSOV is started by placing a point charge, $PC = -1$, at $z=3.2$ a.u. above Ag_{\uparrow}^+ ; this distance is near z_e for both Ag_6F and Ag_7F , see Table X. The E_{INT} for the electrostatic interaction of the fixed SCF orbitals of Ag_{\uparrow}^+ with PC, denoted F.O. Ag_{\uparrow}^+-PC , is 1.5 eV larger for the Ag_7 than for the Ag_6 cluster. This difference must arise from the different 5sp "conduction" band charge distribution for the two clusters. Still representing the F anion by the PC, the Ag_{\uparrow}^+ charge distribution is allowed to polarize in response to the presence of the PC; this step is denoted Pol. Ag_{\uparrow}^+-PC . The Ag_6^+ polarization increases E_{INT} by 3.2 eV while that for Ag_7^+ is increased by 0.7 eV less or 2.5 eV. The larger polarization of the Ag_6^+ cluster leads to an increase of μ by 5.3 a.u. while the increase due to the Ag_7^+ polarization is smaller, 4.8 a.u.. The difference in E_{INT} for Ag_6^+ and Ag_7^+ at Pol. Ag_{\uparrow}^+-PC of 0.8 eV is almost the same difference found at the Full SCF level for Ag_6F and Ag_7F . The difference arises from cancelling F.O. electrostatic contributions due to the distribution of conduction band charge, favoring D_e for Ag_7^+ , and the Ag_{\uparrow}^+ polarization, favoring D_e for Ag_6^+ .

At this point, the Ag_{\uparrow}^+ charge distribution is fixed and the PC is replaced by the fixed, frozen, charge distribution for extended F^- anion; this step is denoted Pol. Ag_{\uparrow}^+-PC/F^- . The Pauli repulsion arising from the non-bonding overlap of Ag_{\uparrow}^+ and F^- charge distributions is large, ~ 2 eV, but is the same for Ag_6F and Ag_7F within 0.1 eV. The following CSOV steps, $V(Ag_{\uparrow}^+,all)$ and $V(F^-,all)$ take account of the full basis set rearrangements of Ag_{\uparrow}^+ and F^- , respectively. The changes in E_{INT} at these steps are very similar for Ag_6F and Ag_7F . Further, the results at $V(F^-,all)$ are close to the Full SCF values for both E_{INT} and μ .

These CSOV show that while the nature of the bonding between clusters and adsorbates is basically independent of cluster shape and nuclearity, the precise values for the chemisorption properties, especially for the D_e , are very cluster dependent. This rules out the possibility to distinguish, on the basis of the present cluster calculations, whether the tetrahedral or the octahedral is the preferred site for halogen chemisorption on Ag (111) surfaces.

V. CONCLUSIONS

The various methods that have been used to characterize the Ag-halogen bond provide consistent evidence that the bond is essentially entirely ionic. They show that a commonly used measure of ionicity obtained from the change in the work function or dipole moment is incorrect because it neglects the metal polarization. The comparison of the interaction of Ag_4^+ with a point charge and with the extended halogen anion shows that there is a large Pauli repulsion opposing the Coulomb attraction and describable as a surface "wall". There is also a large contribution arising from the polarization of the surface charge which is commonly described as an "image charge" effect.²⁹ This surface polarization contributes a large amount not only to the interaction energy but also to the dipole moment. It explains why the work function does not provide a proper measure of the bond ionicity.⁹ The contribution arising from the anion polarization and from the covalent Ag-halogen bonding are much smaller.

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Table I - Extended GTO basis set for halogen atoms^{a)}

	Fluorine		Chlorine		Bromine	
	exp.	coef.	exp.	coef.	exp.	coef.
s	18648.5	.000537	28656.3	.001592	379677.	.000384
	2790.77	.004160	4299.00	.012202	56125.1	.003000
	633.258	.021439	976.335	.060988	12967.3	.014890
	178.599	.083438	274.415	.213429	3836.08	.054774
	57.7896	.240206	89.0063	.453700	1331.99	.156771
	20.4555	.438883	31.2371	.396630	508.042	.332810
	-----	-----	-----	-----	-----	-----
	7.58796	1.0	31.2371	.117005	207.781	.398567
	-----	-----	7.76951	-.35430	90.4218	.176530
	1.99213	.236128	3.07933	-.73910	-----	-----
	.749854	.597574	-----	-----	33.0043	1.0
	-----	-----	3.07933	.523128	14.3563	1.0
	.241845	1.0	.651038	-1.2658	4.72852	1.0
	.09	1.0	-----	-----	2.03297	1.0
			.240798	1.0	.412706	1.0
			.09	1.0	.156141	1.0
					.03	1.0
p	63.1253	.008563	150.436	.028503	3167.91	.002464
	14.5012	.057641	34.7101	.177297	762.504	.019590
	4.38233	.200680	10.4071	.480085	249.396	.091169
	1.45355	.387023	3.37330	.495741	95.2317	.265602
	-----	-----	-----	-----	-----	-----
	.463237	1.0	.748495	1.0	39.9230	.435543
	.126578	1.0	.207855	1.0	17.7816	.311776
	.035	1.0	.058	1.0	-----	-----
					7.67726	.351228
					3.34206	.569853
					-----	-----
					1.44242	1.0
					.442320	1.0
					.137772	1.0
					.03	1.0
d	0.12	1.0	.67	1.0	96.1500	.026513
			.07	1.0	27.8391	.150064
					9.85106	.380489
					-----	-----
					3.61018	.480277
					1.25154	.247885
				-----	-----	
				.06	1.0	

a) The basic basis sets (see text) are taken from Ref. 16-18; they do not contain the most diffuse s, p, and d functions.

Table II - Total energy, E_T , electron affinity (EA) and dipole polarizability (α_D) values for halogen anions computed with basic and extended GTO basis sets.

	F ⁻	Cl ⁻	Br ⁻
$E_T(X^-)$, a.u.			
extended	-99.43819	-459.31400	-2572.16264
BSSE (Ag ₄ -extended) ^a	-99.43885	-459.31954	-2572.16445
Hartree-Fock limit ¹⁹	-99.45937	-459.57670	-2572.53550
EA, eV			
basic	1.37	1.65	2.09
extended	1.35	2.08	2.52
Hartree-Fock limit ¹⁹	1.36	2.58	2.58
experimental ²¹	3.40	3.62	3.36
α_D , Å ³			
basic	0.12	0.12	0.53
extended	1.35	3.77	6.19
BSSE (Ag ₄ -extended) ^a	1.54	4.26	6.32
Hartree-Fock limit ²⁰	1.71	5.89	8.18

^a)The distance of the Ag₄ basis set from the halogen atom corresponds to halogen-Ag surface distances of 3.3, 4.3, and 4.8 a.u. for F, Cl, and Br, respectively.

Table III - Chemisorption properties for halogen atoms on Ag₄ and Ag₁₀ clusters

cluster		Ag ₄ Fa)	Ag ₄ Fb)	Ag ₁₀ Fc)	Ag ₄ Cl a)	Ag ₄ Br a)
z _e	a.u.	3.310	3.289	3.304	4.347	4.721
r _e (Ag-X)	Å	2.42	2.40	2.41	2.84	3.00
μ	a.u.	-1.09	-1.17	-0.37	-1.72	-2.00
ω _e	cm ⁻¹	277	273	255	180	115
ω _e x _e	cm ⁻¹	0.8	0.8	0.9	0.4	0.2
D _e (Ag _n +X)	eV	2.72	2.62	1.92	2.68	2.76
D _e (Ag _n ⁺ +X ⁻)	eV	5.88	5.79	4.56	5.09	4.74

- a) all the Ag atoms are treated with a 19 electron ECP.
b) all the Ag atoms are treated with a 11 electron ECP.
c) the four Ag atoms defining the tetrahedral chemisorption site are treated with a 11 electron ECP; the neighboring Ag atoms are treated with a 1 electron ECP.

Table IV - Projection of X^- on Ag_4X and $Ag_{10}F$ clusters

	Ag_4F	$Ag_{10}F$	Ag_4Cl	Ag_4Br
N_p	9.98	9.98	17.95	35.92
Q_p	-0.98	-0.98	-0.95	-0.92

Table V - Taylor expansion of $\mu(z)$ for Ag_nX and for localized X^- orbitals in Ag_nX ; see Eq.s (3) and (4). All M_i are in a.u..

		Ag_4F	Ag_{10}F	Ag_4Cl	Ag_4Br
$\mu(\text{Ag}_n\text{X})$	M_0	-1.09	-0.37	-1.72	-2.00
	M_1	-1.39	-1.50	-1.60	-1.59
	M_2	-0.09	-0.27	-0.04	-0.01
	M_3	+0.01	+0.07	+0.03	-0.03
$\mu(\text{X})$	M_0	-2.90	-3.00	-3.31	-3.43
	M_1	-1.00	-0.99	-1.10	-1.11
	M_2	+0.10	-0.06	-0.03	-0.04
	M_3	-0.01	+0.04	+0.04	-0.01

Table VI - CSOV analysis for Ag_4F cluster at $z = 3.2$ a.u. (PC = point charge, see text)^a

Step		$E_{\text{INT}}/\Delta E_{\text{INT}}$	$\mu/\Delta\mu$
0. Frozen orbital	PC	+4.82/....	-4.49/....
	F-	+3.37/....	-4.21/....
1. $V(\text{Ag}_4^+, \text{Ag}_4^+)$	PC	+6.92/+2.10	-1.52/+2.97
	F-	+5.25/+1.88	-1.37/+2.84
2. $V(\text{Ag}_4^+, \text{all})$		+5.35/+0.10	-1.43/-0.06
3. $V(\text{F}^-, \text{F}^-)$		+5.59/+0.24	-1.15/+0.28
4. $V(\text{F}^-, \text{all})$		+5.84/+0.25	-1.05/+0.10
5. $V(\text{cov})$		+5.85/+0.01	-1.04/+0.01
6. Full SCF		+5.88/+0.03	-0.94/+0.10

a) Interaction energies, E_{INT} , in eV are computed with respect to separate ions; μ in a.u.

Table VII - CSOV analysis for Ag_4Cl cluster at $z = 4.3$ a.u.
(PC = point charge, see text)^a

Step		$E_{\text{INT}}/\Delta E_{\text{INT}}$	$\mu/\Delta\mu$
0. Frozen orbital	PC	+4.27/....	-5.59/....
	Cl ⁻	+3.11/....	-5.29/....
1. $V(\text{Ag}\uparrow, \text{Ag}\uparrow)$	PC	+5.47/+1.20	-3.03/+2.56
	Cl ⁻	+4.10/+0.99	-2.90/+2.39
2. $V(\text{Ag}\uparrow, \text{all})$		+4.16/+0.06	-2.96/-0.06
3. $V(\text{Cl}^-, \text{Cl}^-)$		+4.54/+0.38	-2.32/+0.64
4. $V(\text{Cl}^-, \text{all})$		+5.01/+0.47	-2.05/+0.28
5. $V(\text{cov})$		+5.04/+0.03	-2.00/+0.05
6. Full SCF		+5.09/+0.06	-1.64/+0.35

a) Interaction energies, E_{INT} , in eV are computed with respect to separate ions; μ in a.u.

Table VIII - CSOV analysis for Ag_4Br cluster at $z = 4.8$ a.u.
(PC = point charge, see text)^a

Step		$E_{\text{INT}}/\Delta E_{\text{INT}}$	$\mu/\Delta\mu$
0. Frozen orbital	PC	+4.04/....	-6.01/....
	Br^-	+2.99/....	-5.93/....
1. $V(\text{Ag}^+, \text{Ag}^+)$	PC	+4.97/+0.93	-3.73/+2.28
	Br^-	+3.76/+0.77	-3.72/+2.21
2. $V(\text{Ag}^+, \text{all})$		+3.80/+0.03	-3.76/-0.04
3. $V(\text{Br}^-, \text{Br}^-)$		+4.14/+0.35	-3.10/+0.66
4. $V(\text{Br}^-, \text{all})$		+4.65/+0.50	-2.65/+0.45
5. $V(\text{cov})$		+4.67/+0.02	-2.58/+0.07
6. Full SCF		+4.74/+0.07	-2.21/+0.46

a) Interaction energies, E_{INT} , in eV are computed with respect to separate ions; μ in a.u.

Table IX - Equilibrium bond distances in a.u. for halogens chemisorbed on Ag_4 in the presence of an external field F (in a.u.). Both Stark and variational SCF values are given

F		Ag_4F $z_e/\Delta z$	Ag_4Cl $z_e/\Delta z$	Ag_4Br $z_e/\Delta z$
0.00	SCF	3.310/.....	4.347/.....	4.721/.....
+0.01	Stark	3.098/-0.21	4.055/-0.29	4.405/-0.32
	SCF	3.092/-0.22	4.058/-0.29	4.418/-0.30
-0.01	Stark	3.637/+0.33	4.893/+0.55	5.375/+0.65
	SCF	3.620/+0.31	4.904/+0.56	5.410/+0.69

Table X - Chemisorption properties for F atom on Ag₆ and Ag₇ clusters^{a)}

cluster		Ag ₆ F	Ag ₇ F
Bare Ag _n clusters			
IP	eV	5.54	4.31
$\mu(\text{Ag}_n)$	a.u.	0.06	-0.26
$\mu(\text{Ag}_n^+)$	a.u.	-2.10	-3.09
Ag ₆ F and Ag ₇ F clusters			
Z_e	a.u.	3.333	3.291
ω_e	cm ⁻¹	252	273
$D_e(\text{Ag}_n+\text{X})$	eV	0.44	2.48
$D_e(\text{Ag}_n^++\text{X}^-)$	eV	4.60	5.41
Q_p		-0.98	-0.98
$\mu(\text{Ag}_n\text{F})$	M_0	-0.02	-1.16
	M_1	-1.05	-1.53
	M_2	-0.41	-0.15
	M_3	+0.09	+0.04
$\mu(\text{F}^-)$	M_0	-3.04	-3.00
	M_1	-0.99	-0.96
	M_2	-0.05	-0.04
	M_3	+0.00	-0.01

a) the three surface Ag atoms are treated with a 11 electron ECP; the remaining Ag atoms are treated with a 1 electron ECP.

Table XI - CSOV analysis for Ag_6F and Ag_7F clusters at $z = 3.2$ a.u. (PC = point charge, see text)^a

Step	Ag_6F		Ag_7F	
	$E_{\text{INT}}/\Delta E_{\text{INT}}$	$\mu/\Delta\mu$	$E_{\text{INT}}/\Delta E_{\text{INT}}$	$\mu/\Delta\mu$
F.O. Ag^+-PC	+2.56/....	-5.30/....	+3.99/....	-6.29/....
Pol. Ag^+-PC	+5.72/....	+0.04/....	+6.52/....	-1.54/....
Pol. $\text{Ag}^+-\text{PC}/\text{F}$	+3.77/-1.95	+0.24/+0.20	+4.65/-1.87	-1.37/+0.17
$V(\text{Ag}^+, \text{all})$	+3.90/+0.13	-0.14/-0.38	+4.74/+0.09	-1.40/-0.03
$V(\text{F}^-, \text{all})$	+4.55/+0.65	+0.13/+0.27	+5.39/+0.64	-1.12/+0.28
Full SCF	+4.60/+0.05	+0.11/-0.02	+5.41/+0.02	-1.13/+0.09

a) Interaction energies, E_{INT} , in eV are computed with respect to separate ions; μ in a.u.

Figure 1. Schematic representation of the $\text{Ag}_4(3,1)\text{X}$ $\text{X}=\text{F}, \text{Cl}, \text{Br}$, and of the $\text{Ag}_{10}(3,7)\text{F}$ clusters modeling the tetrahedral site on the $\text{Ag}(111)$ surface. The halogen atom is above the center of the triangle formed by the three Ag surface atoms.

Figure 2. Schematic representation of the $\text{Ag}_6(3,3)\text{F}$ and of the $\text{Ag}_7(3,3,1)\text{F}$ clusters modeling the octahedral site on the $\text{Ag}(111)$ surface. The halogen atom is above the center of the triangle formed by the three Ag surface atoms.